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(54) **Use of silylesters of rosin in self-polishing antifouling paints**

(57) Silylesters of rosin are used in self-polishing antifouling paints alone or in combination with other binder components.

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## Description

[0001] The present invention relates to binders for self-polishing antifouling paints. More particularly, it relates to the use of silylestere as binder in self-polishing antifouling paints.

[0002] Many existing antifouling paints used for ships to prevent barnacles and other marine life from attaching to the ships' hulls work by slowly leaching metallic compounds into the sea. But studies have shown that these compounds persist in the water, killing sea life, harming the environment and possibly entering the food chain. One of the most effective types of antifouling paint, developed in the 1960s, contains the organotin tributyltin (TBT), which has been proven to cause deformations in oysters and sex changes in whelks.

[0003] The International Maritime Organization (IMO), a unit of the United Nations, adopted on 5 October 2001 an International Convention on the Control of Harmful Antifouling Systems at the end of a five-day Diplomatic Conference held in London.

[0004] The proposed antifouling convention comes in response to Assembly resolution A.895 (21) (Antifouling systems used on ships, adopted by IMO in November 1999, which called on IMO's Marine Environment Protection Committee (MEPC) to develop an instrument, legally binding throughout the world, to address the harmful effects of antifouling systems used on ships).

[0005] The resolution calls for a global prohibition on the application of organotin compounds which act as biocides in antifouling systems on ships by 1 January 2003, and a complete prohibition on the presence of organotin compounds which act as biocides in antifouling systems on ships by 1 January 2008.

[0006] The harmful environmental effects of organotin compounds were recognized by IMO in 1990, when the MEPC adopted a resolution which recommended that Governments adopt measures to eliminate the use of antifouling paint containing TBT on non-aluminium hulled vessels of less than 25 meters in length and eliminate the use of antifouling paints with a leaching rate of more than 4 micrograms of TBT per day. Some countries, such as Japan, have already banned TBT in antifouling paint for most ships.

[0007] There is therefore a need in the art for improved erodable antifouling paint compositions containing no organotin compound, while retaining the good antifouling and self-polishing properties of the tin-containing antifouling paints of the prior art.

[0008] Tin-free systems are well known in the art:

- Antifouling paints containing rosin and similarly soluble salts thereof exist for many years. Rosin is slightly soluble in seawater ( $8.6 \times 10^{-5}$  mol/L at pH = 8.1). Due to its low molecular weight, rosin is blended with another binder to provide an appropriate film-forming performance.
- Paints based on a combination of wood rosin with copper- or zinc-pyrithione have been found to thicken or gel unacceptably within a few days. US 5,112,397 (Olin Corp.) discloses paints containing an amine compound or esterified wood rosin to impart desired gelation-inhibition.
- EP 289481 and EP 526441 (Sigma Coatings), WO 9744401 (Hempel's) disclose systems based on rosin in combination with a film forming binder. However, the coatings produced in accordance with these specifications suffer from the technical problem that their coatings are nowadays classified as "ablative" since the erosion is not based on a real chemical hydrolysis but well on a complex process which weakens the surface layer by a combination of dissolving and leaching followed by frictional abrasives forces leading to higher surface roughness (at micron scale ablative pattern) and an irregular erosion rate of the coating.
- Systems based on copper (or zinc) acrylates are described in EP 342276 (Nippon Paint), GB 2 311 070 (Kansai Paint), US 5 545 823 and US 5 382 281 (Yung Chi Paint). Based on cheap raw materials these tin-free systems suffer from several drawbacks. Indeed, their production requires a dedicated equipment and their composition is very difficult to assess by chemical analysis. Further, the use of copper in antifouling systems will certainly be restricted in the forthcoming years. An example of that trend is the Dutch ban on the application of copper-containing antifouling paints on yachts smaller than 25 meters.
- Systems based on silyl acrylates were disclosed by M&T (WO 8402915, EP 00131621), and further developed by Chugoku (EP 775733), Nippon Oils & Fats (EP 297505, EP 646630, EP 714957, EP 802243) and Sigma Coatings (WO 0162811 and WO 0162858)

[0009] It is known in the art that rosin or rosin derivatives may be used in combination with hydrolysable acrylates in order to improve some of their properties.

[0010] EP 530205 (Courtaulds) discloses the use of rosin amine D in combination with copper acrylates.

WO 0043460 (Akzo Nobel) discloses some advantages of using blends of rosin (and its derivatives) with zinc/copper acrylates.

[0011] EP 1016681 (Chugoku) discloses that the blending of rosin (and its derivatives) with trialkylsilyl(meth)acrylate co-polymers improve the ability to erode at static conditions (e.g. during the outfitting period in the building of new ships) and by this having a superior antifouling performance. The recoatability and the resistance to cracking and detachment were also claimed to be improved by this blending

[0012] EP 802243 (Nippon Oils & Fats) discloses blends of at least one compound selected from rosin, rosin derivatives and rosin metal salts with certain polymers containing organosilyl ester groups as binder in self-polishing antifouling paints, leading to improved properties after long-term immersion.

Nowadays, the ship owners continue to request an excellent performance over increasingly longer periods of time, in order to reduce the frequency of dry-docking the ships to apply a fresh coating on their hulls. There is thus a continuous need in the art for alternative and improved self-polishing antifouling paint compositions.

[0013] The inventor has surprisingly found that the "ablative" effect of the antifouling paints based on rosin or rosin metal salts could be largely overcome by using silylesters of rosin (alternatively called silylated resins or silyl abietates).

[0014] Thus the present invention provides the use in self-polishing antifouling paints of silylesters of rosin as binder component of the binder system.

[0015] For the purpose of this specification, the term "binder system" means a composition consisting essentially of silylesters of rosin and optionally other binder components well known by the man of the art.

[0016] The present invention provides also a process for preparing self-polishing antifouling paints characterised in that one step of the process is the addition of silylesters of rosin as binder component of the binder system.

[0017] The invention is based on the recognition that the self-polishing properties of antifouling paints containing rosin were insufficient due to the presence of free carboxylic groups on the rosin; said properties being unexpectedly found to be greatly improved after reaction of the free carboxylic group of rosin with a silyl group.

[0018] Rosin is a loosely used term, denoting the result of a harvesting of the gum exudations from surface cuts made in certain species of trees. Rosin is sometimes defined restrictively as the product obtained from pines; similar products comprised in the generic term "rosin" as used herein include Congo copal, Kauri copal, Damar and Manilla gums. Other processes for obtaining rosin include dissolving wood rosin from pine stumps after forests have been felled, or refining a by-product of the kraft paper manufacturing process to produce tall oil rosin.

Pine-originating rosin is preferably chosen. The main component (about 80 %) of rosin is abietic acid, also called sylic acid (CAS RN. = 514-10-03), which could be used instead of rosin.

[0019] The silylester of rosin in this invention can also be a silylester of a rosin derivative.

In the present context the term "rosin derivative" is intended to mean all types of rosin (as defined above) modified or derivatised according to various chemical reactions or processes which leave at least one carboxylic acid group per molecule available for silylation. A number of processes are expected to lead to rosin derivatives which have superior paint constituent properties with respect to improvement of the mechanical properties and/or control of the self-polishing properties.

[0020] As examples, one can cite:

- A. the adducts of unsaturated acids (such as acrylic acid, maleic acid or fumaric acid)-and the mono-esters of diacids with rosin.
- B. adducts of rosin itself (dimerised rosin, oligomerised or polymerised rosin)
- C. hydrogenated or partially hydrogenated rosin
- D. dismutated or disproportionated rosins

[0021] A more extensive description of rosin and rosin derivatives can be found in WO 9744401 (Hempel's).

[0022] Commercially available examples of some rosin and rosin derivatives are given in Table 1. Most of these examples have high softening points and have therefore no adhesive properties.

Table 1:

Commercially available examples of rosin derivatives.				
Description	Trade name	Company	Acid number	Softening (°C)#
Portuguese gum rosin	(rosin)	Demonchi	170	70
Hydrogenated rosin	Foral AX-E	Hercules	170	80

#By ring and ball method according to ASTM-E28

Table 1: (continued)

Commercially available examples of rosin derivatives.				
Description	Trade name	Company	Acid number	Softening (°C)#
Dimerized rosin	Dymex	Hercules	145	150
Partially polymerized rosin	Poly-Pale	Hercules	140	102
Acid modified ester	B106	Hercules	200	183
Maleic anhydride ester	K1614	Lawter	200	160
Fumarated rosin	Ennesin FM6	Lawter	305	140

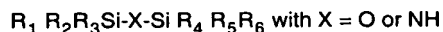
#By ring and ball method according to ASTM-E28

[0023] The reaction of carboxylic acid groups with substituted silyl groups is well known in the art; see e.g.

- J.D. Nicholson in The Analyst. vol. 103, n°1224, pp 193-222 (March 1978)
- M. Lalonde, T.H. Chan in Synthesis pp 817-845 (September 1985)

[0024] The preparation and gas chromatography of the trimethylsilyl ester of rosin (CAS RN=21414-50-6) was reported (J. Gas Chromatogr. 1968, 6 (3) 158 - 160).

Examples of silylating agents are triorganosilyl chlorides and hydrides, and hexaorgano disiloxanes and disilazanes :



[0025] According to the invention, the silicon substituents are alkyl radicals, which may be the same or different, including methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, t-butyl and phenyl. An example of silylating agent with different substituents is dimethyl t-butyl silyl chloride. The preferred substituents are methyl and ethyl, more preferred substituents being methyl.

[0026] According to another preferred embodiment, di-, tri-, tetrafunctional silylating agents and mixtures thereof can also be used, for example dimethylsilyl dichloride, ethylsilyl trichloride and tetrachlorosilane, to obtain respectively dialkylsilyl diresinate, alkylsilyl triresinate, silyl tetraresinate and mixtures thereof.

[0027] An object of the present invention is the use in self-polishing antifouling paints of silylesters of rosin as binder component of the binder system wherein the silylesters of rosin are in an amount of from 5 to 100% by weight, based on the total weight of the binder system composition.

[0028] According to an embodiment, the silylesters of rosin are used in an amount of from 5 to 25% by weight, based on the total weight of the binder system composition.

[0029] According to another embodiment, the silylesters of rosin are used in an amount of from 35 to 65% by weight, based on the total weight of the binder system composition.

[0030] According to yet another embodiment, the silylesters of rosin are used in an amount of 100% by weight, based on the total weight of the binder system composition.

[0031] The inventor has now surprisingly found that the complete conversion of the acid functionality of rosin compounds into a silylester has many advantages for paint formulation, manufacturing and stability by providing a silyl ester that is :

- Inert to reactive pigments such as zinc oxide and cuprous oxide. It is well known that self-polishing antifouling paints containing rosin compounds react through their free acid functionality with reactive pigments, in practice always present in antifouling paints, such as zinc oxide or cuprous oxide, to form the corresponding salts e.g. zinc resinate or cuprous resinate. The metal salts of resins have the disadvantage of being hardly soluble in seawater and having poor adhesive and film forming properties.
- Inert to biocides. There is for example no more risk of gelation that usually occurs when zinc/copper pyrithione is used in rosin-based formulations. It is well known that zinc pyrithione is one of the modern biocides used in antifouling paints but that it has the disadvantage of being unstable in the presence of carboxylic acid groups and/or the metal salts of carboxylic acid groups. This biocide can therefore e.g. not without special precautions be used

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in rosin-based paints because they always do contain carboxylic acid groups to some extent which lead to an irreversible gelation of the paint.

- More sensitive to dissolving and erosion processes in water (fresh water or seawater).
- Less brittle; in other words having a lower glass transition temperature (T<sub>g</sub>) and softening point than corresponding metal salts of the resinate species concerned.

[0032] Indeed, whilst the reaction of rosin compounds with zinc oxide or cuprous oxide has the effect of increasing the softening point and the T<sub>g</sub> as well, e.g. softening point from 70 °C for rosin to 160 °C for zinc resinate. In contrast there is hardly an increase when the acid function of rosin compounds has reacted with a silyl group according to the invention (e.g. T<sub>g</sub> values in example 1: from 52 °C for rosin to only 62 °C for trimethylsilyl resinate).

[0033] The hydrolysable silylestere of rosin can be used as sole resin or preferably in combination with other binders to form a binder system that are commonly in use in antifouling formulations. When other binders are present, those are in an amount of from more than 0 up to 95% by weight, based on the total weight of the binder system composition.

Examples of other binders are:

[0034]

- Resinates of Ca, Cu or Zn
- Naphthenates of Ca, Cu, Zn
- Vinyls like Laroflex MP (commercially available from BASF)
- Acrylates like Neocryl B725 (commercially available from Avelia)
- Cu/Zn/Ca acrylates, e.g. as described in EP 342276; EP 982324 (Kansai) or polyesters e.g. as described in EP 1033392 (Kansai).
- Tri-organosilyl(meth)acrylates copolymers as described e.g. in EP 131626 (M&T); US 4593055 (M&T); EP 775773 (Chugoku); EP 646630 (NOF); US 5436284 (NOF); WO 0162811 and WO 0162858 (SIGMA COATINGS).
- Hydrophilic (meth) acrylates such as e.g. described in FR 2 557 585 (Jotun), EP 526441 and EP 289441 (SIGMA COATINGS). It has been observed that blends of the hydrophilic acrylic resins such as described in EP 526441 and EP 289441 with a silylester of rosin had improved properties over blends with zinc resinate. The film was more flexible, had better adhesive properties and showed a hydrolysis-driven erosion process at pH 12 while not showing defects upon immersion in fresh and sea water conditions (pH 7 and 8 respectively).

[0035] The following non-limiting examples illustrate the invention. The measuring methods used in the examples are given further.

Example 1 : synthesis of trimethylsilyl resinate

[0036] 420 g Portuguese gum rosin was put in a 2-L 4-necked flask and kept under nitrogen. The four necks of the flask were equipped with stirring means, a reflux cooler, a thermometer for temperature control of the reaction, and means for addition of the reactants. The gum rosin was dissolved in a solvent mixture of 218 g xylene and 850 g toluene. Here after 128 gram triethylamine was carefully added in 5 minutes under vigorous stirring. As a consequence the temperature of the contents of the flask rose by 10°C. The addition of the tri-ethyl amine was followed by the slow addition of 138 g trimethylsilyl chloride under vigorous stirring.

[0037] A white salt was instantaneously formed and the exothermic reaction made the contents raise to a temperature of 50°C. The reaction mixture was kept at a temperature of 50°C for 5 hours. Then the heating and the stirring was stopped. The next day the formed trimethylsilyl resinate was purified by filtration and evaporation of the toluene solvent fraction. The yield was 530 g (circa 78 %) of a brown colored solution, that was 75 wt % in solids and had a viscosity of 3 dPa.s. The binder was very flexible and had a good adhesion on glass and epoxy primer and showed hydrolysis within minutes upon immersion in an alkaline solution of pH 12. This all in contrast with zinc resinate which had a hard and brittle film with moderate adhesion on glass and without showing any hydrolysis behavior up to pH 13. The binder had a T<sub>g</sub> of 62 °C.

Example 2 : synthesis of dimethylsilyldiresinate

[0038] The same equipment and procedures were used as for the synthesis of example 1 with the following differences:

335 g Portuguese gum rosin had been dissolved in 121 g xylene and 500 g toluene.

To this had been added consecutively 101 g tri-ethyl amine and 64,5 g dimethyldichlorosilane.

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The yield was 300 g of a brown colored solution that was 70 wt % in solids and had a viscosity of 10 dPa.s.

The binder had a good adhesion on glass and epoxy primers.

The binder was very sensitive to alkaline hydrolysis. A binder film dissolved in water of pH 12 completely within 15 minutes.

The binder had a Tg of 52 °C.

[0039] Some properties of trimethylsilyl resinate and dimethylsilyl resinate are specified in table 2.

[0040] Examples 1 and 2 demonstrate that silylesters of resinates dissolve in alkaline solutions more quickly than for example zinc resinate and that they are less brittle than zinc resinate.

Table 2 :

Parameter	Trimethylsilyl-resinate (ex 1)	Dimethylsilyl-diresinate (ex 2)	Zinc Resinate	Rosin
Tg (°C)	62	52	160	52
Dissolving (at pH)	Yes (pH 12)	Yes (pH 12)	No (pH 13)	Yes (pH 12)

Paint Formulas : Examples 3 to 6 and comparative example A.

[0041] Several paints were prepared whose composition by weight is given in Table 3.

Table 3 :

Paint compositions						
	Example →	3	4	5	6	A
Ingredients	Description	wt%	wt%	wt%	Wt%	wt%
TrimethylSiresinate	75 wt % in xylene (ex. 1)	24.1				
DimethylSidiResinate	70 wt % in xylene (ex. 2)		27.5	12.5	2.5	
50MA/25VP/25BA				17.4		17.4
Zinc resinate	Erkacit 250				10.9	8.7
Laroflex MP 45	Vinylchloride (BASF)				4.9	
Thix. Agents		1.3	1.4	1.3	1.3	1.3
Cuprous oxide		40.2	42.1	38.4	38.4	38.5
Zinc oxide		15.0	7.9	14.3	14.3	14.4
Iron oxide		6.7	7.0	6.4	6.4	6.4
Zinc pyrithione	Zinc Omadine (Arch)		2.8			
Xylene		12.6	11.2	9.7	21.3	13.3
Total		100.0	100.0	100.0	100.0	100.0

[0042] In Example 5 and Comparative Example A, there was used a solution (50 wt % in xylene) of resin 50MA/25VP/25BA according to example 1 of EP-A-526 441, having the monomer weight composition 50 % methyl acrylate, 25 % vinyl pyrrolidone and 25 % butyl acrylate. In Comparative Example A, there was used zinc resinate. The amount by weight of the silylesters of rosin, based on the total weight of the binder system, used in the several paint formulas is given in table 4

Table 4

	3	4	5	6	A
Ingredients	wt%	wt%	wt%	wt%	wt%
TrimethylSiresinate	100				-
DimethylSidiResinate		100	50.1	10	-

[0043] Properties of the paints are presented in Table 5.

Table 5 :

Paint properties						
Properties	Units (parameters)	3	4	5	6	A
Viscosity	dPa.s	12	15	13	15	11
Can Stability	(3 months; 20 °C)	ok	ok	ok	Ok	ok
Erosion rate	µm/month (average during 12 months)	7	12	5	4	3
Fouling (1 season)	% (fouled area)	0	0	0	3%	10 %

[0044] None of the paint formulas did show any significant raise in viscosity upon 3 months storage at 20°C.

The paints have been tested for antifouling activity and erosion rate.

Paints according to the invention present outstanding antifouling and self-polishing properties.

No significant weed or animal fouling has been observed on the panels coated with the paints according to the invention and the algal slime was practically non-existent.

[0045] Measuring methods used in the examples are as follows :

#### Determination of the solids content

[0046] The solids content was determined by weighing before and after heating a sample for 1 hour at 120°C [standard test methods ISO 3233/ASTM 2697/DIN 53219].

#### Determination of the viscosity

[0047] The viscosity of binder solutions and of paints was determined with a Brookfield at 25°C [ASTM test method D2196-86].

The viscosity of paints had been adjusted between 10 and 20 dPa.s. with xylene. The viscosity was measured using a Haake VT 181 (body E30 or 100) viscosimeter under standard conditions.

#### Evaluation of the hydrolysability of the binders

[0048] The hydrolysability has been evaluated by dipping draw-downs in an alkaline solution (NaOH, pH 12.0 - 13.4). Hydrolysability is reported as "yes" at a certain pH when hydrolysis or complete dissolving of a film (50-100 µm) could be observed within one hour.

#### Determination of the softening point

[0049] The ring and ball method according ASTM-E28 was used.

#### Determination of the Tg of the binders

[0050] Samples for the actual determination were made by making draw downs of the resins on glass and drying for 16 hours at 120 °C. Here after the measurements had been carried out with a differential scanning apparatus of TA instruments, DSC10 according ASTM 3418.

#### Evaluation of the polishing of paints

[0051] The erosion rate is the average decrease in film thickness (expressed in µm/month) per month over the whole test.

Stainless steels discs, 20 cm in diameter, were protected with a standard anti-corrosive system (300 µm in dry film thickness). Two layers of the self-polishing paint to be tested were applied, to give a total dry film thickness between 200 and 300 µm. The tests were carried out in constantly refreshed natural seawater, at a constant temperature of 20 °C. The discs were rotated at 1000 rpm, corresponding to about 34 km/h (18 knots) at 9 cm from the center. The total dry film thickness was determined at 2 monthly intervals, after allowing the paint to dry during one day. It was measured at a number of fixed points, each located at 9 cm from the center of the discs.

The evaluation of the antifouling activity of the paints.

[0052] The antifouling activity was tested by applying the prepared paints to a plaque over a vinyl resins/tar anti-corrosive paint, mounting the plaque on a panel and immersing the panel from a raft in a river estuary off the Southern Netherlands during the active season (March → October). Each test also included plaques coated with a non-toxic control (which became heavily fouled with seaweed and some animal life within 4 weeks). The fouling rate is reported by stating the area covered with fouling.

**Claims**

1. Use in self-polishing antifouling paints of silylesters of rosin as binder component of the binder system.
2. Use according to claim 1 wherein the silylesters of rosin are in an amount of from 5 to 100% by weight, based on the total weight of the binder system.
3. Use according to claim 1 wherein the silylesters of rosin are selected from the group consisting of trialkylsilyl monoresinate, dialkylsilyl diresinate, alkylsilyl triresinate, silyl tetraresinate and mixtures thereof.
4. Use according to claim 3 wherein the silyl alkyl substituents are selected from the group consisting of methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, t-butyl and phenyl substituents and mixtures thereof.
5. Use according to claim 4 wherein the silyl alkyl substituents are selected from the group consisting of methyl and ethyl substituents and mixtures thereof.
6. Use according to claim 5 wherein the silyl alkyl substituents are selected from the group consisting of methyl substituents.
7. Use according to anyone of the preceding claims wherein silylesters of rosin are used in combination with other binder components.
8. A process for preparing self-polishing antifouling paints **characterised in that** one step of the process is the addition of silylesters of rosin as binder component of the binder system.





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## EUROPEAN SEARCH REPORT

Application Number

EP 01 20 4141

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The present search report has been drawn up for all claims			
Place of search <b>THE HAGUE</b>		Date of completion of the search <b>13 March 2002</b>	Examiner <b>Miller, A</b>
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

EPO FORM 1503 03 82 (P/C/C1)

**ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.**

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This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on  
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